SIMULATION AND ENVIRONMENTAL ASSESSMENT OF BIODIESEL USING SUPERCRITICAL METHANOL

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A proposal submitted in fulfillment of the

Requirements for completing the assessment of

Final Year Project (PSM 2)

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FEBRUARY 2013

SUPERVISOR'S DECLARATION

I hereby declare that I have checked this thesis and in my opinion, this thesis is adequate in terms of scope and quality for award of the Degree of Chemical Engineering.

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Position:

Date:

STUDENT DECLARATION

I hereby declare that the work in this thesis is my own except for the quotations and summaries which have been duty acknowledge. The thesis has not been accepted for any degree and is not currently submitted for award of other degree.

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DEDICATION

Special dedicated to my beloved Father, Mother

Brothers and Sister

My future Wife

Professors, Lecturers and Friends…..

Special Thanks for all of you Care, Love, Encouragement and Best Wishes.

ACKNOWLEDGEMENT

In the name of Allah, Most Gracious, Most Merciful. First and foremost, I would like gratitude and praises goes to ALLAH, in whom I have put my trust and faith in. With the help and blesses from the Almighty, all the obstacles and problem have solved smoothly.

I also would like to take this opportunity to express profound gratitude to my research supervisor, Dr. Ing Mohamad Rizza bin Othman for the excellent guidance and valuable experience along the process to complete this research. His patience, time, thoughts and understanding are highly appreciated.

I am very thankful to community of University Malaysia Pahang (UMP) for providing good facilities in the campus for my studies and run thesis during this four year finishing my engineering degree.

My sincere appreciation also extends to all my fellow colleagues; their help, support and understanding are really appreciated. Last but not least, I would like to thank my beloved family who always being supportive, helpful and listened to all my doubt and problems during my study. All their helped will always remembered.

ABSTRACT

Biodiesel is a recommended petroleum-based diesel substitute mainly because it is environmentally friendly and is renewable, domestic resource. In this thesis, supercritical methanol process to produce biodiesel from the rapeseed was design and simulate by using Aspen Plus v 7.0. Process flowsheets, along with detailed operating conditions and equipment design for this process was created. An environment assessment was also performed based on the result of process simulations and compare with heterogeneous catalyst method. WAR algorithm method is applied to perform environment assessment. The simulation results showed the supercritical process with 42:1 molar ratio and working at 350^0C and 430 bar produce 997.91kg/h of FAME. . The environmental impact assessment shows the heterogeneous catalyst process show the least PEI result compare to supercritical methanol process which is indicate TRO 1552.33(with product) and TRO 1668.01(with product) respectively.

ABSTRAK

Biodiesel merupakan pengganti diesel berasaskan petroleum yang disyorkan terutamanya kerana ia adalah mesra alam dan boleh diperbaharui serta sumber domestik. Dalam tesis ini, Aspen Plus v 7.0 digunakan untuk process simulasi berasaskan biji sawi untuk menghasilkan biodiesel melalui process superkritikal methanol. Diagram proses, serta keadaan operasi yang terperinci dan reka bentuk peralatan untuk proses ini telah dicipta. Melalui penilaian teknikal proses ini menunjukkan bahawa dengan menggunakan metanol superkritikal, ia menghasilkan product yang tinggi dan jangka masa process adalah singkat. Satu penilaian persekitaran juga telah dilakukan berdasarkan hasil simulasi proses dan perbandingan kaedah heterogeneous catalyst dibuat untuk tujuan pembelajaran. Kaedah WAR algoritma digunakan untuk penilaian alam sekitar. Keputusan simulasi menunjukkan proses ini dengan nisbah molar 42:1 dan beroperais pada 350^0C dan 430 bar berjaya menghasilkan 997.91kg/Jam biodiesel. Berdasarkan keputusan kajian alam sekitar, keputusan menunjukkan bahawa kaedah heterogeneous adalah paling kuranng kesan terhadap alam sekitar berbanding dengan kaedah superkritikal methanol dengan menunjukkan bacaan masing-masing pada TRO 1552.33(produk) dan TRO 1668.01(produk).

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LIST OF ABBREVIATION

WAR	-	Waste Reduction
ASTM	-	American Society for Testing and Materials
FAME	-	Fatty Acid Methyl Esters
FFA	-	Free Fatty Acids
SCM	-	Supercritical Methanol Method
PEI	-	Potential Environment Impact
GWP	-	Global Warming Potential
ODP	-	Ozone Depletion Potential
AP	-	Acidification Or Acid Rain Potential
PCOP	-	Photochemical Oxidation
HTPI	-	Human Toxicity By Ingestion
HTPE	-	Human Toxicity By Inhalation Or Dermal Exposure
ATP	-	Aquatic Toxicity Potential
TTP	-	Terrestrial Toxicity Potential
TRO	-	Total Rate Output

CHAPTER 1

INTRODUCTION

1.1 Background of study

Biodiesel refers to a vegetable oil or animal fat-based diesel fuel consisting of long-chain alkyl esters. Typically, it made by chemically reacting lipids such as vegetable oil, animal fat with an alcohol to produce fatty acid esters (Zhang *et al.*, 2002). Biodiesel used in standard diesel engines and it is derived from the vegetable and waste oils used to fuel converted diesel engines. Biodiesel can be used alone, or blended with petro diesel. Because its primary feedstock is a vegetable oil or animal fat, biodiesel is generally considered to be renewable. Since the carbon in the oil or fat originated mostly from carbon dioxide in the air, biodiesel is considered to contribute much less to global warming than fossil fuels. Homogeneous acid and alkali process design are conventional methods that are widely used in industry. However, heterogeneous catalysis and supercritical methanol process have been reviewed to show advantageous over the conventional process.

In this paper, based on study done by Othman *et al.* (2011) a biodiesel production plant was developed using supercritical methanol and acid oils as raw materials. A process simulator was employed to produce the conceptual design and simulate using Aspen Plus software. By using these models also, it was possible to perform environmental assessment. The supercritical alternative appears as a good technical possibility to produce biodiesel.

1.2 Problem statement

Environmental assessment was rarely introduced in a process design. Environmental concern received more attention in recent years thus implementing environmental assessment is an advantage in process design.

In environmental assessment of process design, common environmental performance used was LCA which was time consuming and costly. Alternatively, WAR algorithm was used as it is best performed during designing stage due to the simpler approaches (Othman *et al.*, 2011). Environmental assessment using WAR algorithm method determined the potential environmental impact (PEI) through a process thus help to evaluate the effect that the mass of the process would have on the environment if they were to be emitted to the environment.

1.3 Research objectives

1. Simulation and modeling of biodiesel via supercritical system using Aspen Plus software

2. To evaluated environmental assessment using waste reduction analysis (WAR) algorithms

1.4 Scopes of the proposal study

In this study, continuous process of biodiesel production at a rate of 8000 tonnes/year using supercritical methanol is modeled and simulated based on the design and parameters referred from Lim *et al*. (2009) and Othman et al. (2011). Results from simulation are then used to perform economic and environmental analysis. The scopes of this study include:

i. Develop and modeling the continuous process flowsheets of supercritical biodiesel process using Aspen Plus V7.0
ii. Determine the potential environment impact (PEI) of biodiesel process using WAR algorithm method performed in spreadsheet of Microsoft Excel.

1.5 Significance of the Proposed Study

The significance of this study is to provide another perspective of analyzing process design which is by taking account the environmental criteria. Analyzing of potential environmental impact (PEI) in process design improved the economic and environmental aspect of the process itself.

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1.6 Thesis Structure

This thesis consist five chapters which is the introduction, literature review, methodology, result and discussion, and conclusion and recommendation.

Chapter one is divided into six sub chapters which are background of proposed study, problem statement, research objective, scope of the proposed study, significance of the proposed study and thesis structure.

The second chapter consists of introduction, process description, and technology option for biodiesel production, supercritical methanol, and Environment Assessment.

The third chapter is methodology that consist seven part which are introduction, process synthesis, process simulation, chemical component, thermodynamics method and model, process flowsheet diagram, and Environmental assessment.

The fourth chapter is result and discussion. The chapter contains five chapters which are introduction, simulation results, discussion, Environmental assessment and simulation difficulties

For the chapter five is about result and recommendations.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Biodiesel is a renewable and environmentally friendly energy. It is also an important replace for petroleum diesel. According ASTM biodiesel can be defined as monoalkyl ester of long chain fatty acids derived from a renewable lipid feedstock, such as vegetable oil or animal fatty. It is typically produced by a catalyzed transesterification reaction in which vegetable oil or animal fatty reacts with an alcohol. As an alternative, biodiesel can be in the neat form or mixed with petroleum-based diesel.

Relative conventional petroleum-based fuels, biodiesel has gained acceptance as an alternative fuel because:

- It is renewable, domestic resources. Every country has ability to produce biodiesel because it derived from the vegetable oil and animal fat. Thus it will reduce import of petroleum-based diesel.
- It is biodegrable and non-toxic. According to the European test of biodiesel produced from the rapeseed oil shows that it is 99.6% biodegrable within 21 days and should completely within one month (Congressional Research Service, 1993).
- It produces less carbon monoxide, lower particular matter (e.g smoke), unburned hydrocarbons (e.g soot) and almost no sulfur or aromatic compounds compared to the petroleum diesel. For an engine running on the biodiesel, found a 20% reduction in carbon monoxide emissions (Korbitz *et al.* 1999), 99% reduction in sulfur compounds, and 45% reduction in particulate matter and soot emissions.

- It has a high flash point (approximately 150^0C). Petroleum-based diesel has a much lower flash point (approximately 50^oC) (Krawczyk *et al.* 1996). Fuels with higher flash points are less volatile and thus, it will safer to transport or handle.

Apart from these good features, biodiesel has some limitations:

- It has poorer low-temperature properties (e.g, higher cloud point) than petroleum-based diesel fuels, which might be a barrier to its use in cold climates. One effective way to overcome this shortcoming is to produce a blend of biodiesel with petroleum-based diesel fuels, such as B20 (20% biodiesel, 80% diesel) (Krawczyk *et al.,* 1996).
- It has slightly higher (3%) emissions of nitrogen oxide (NO_2) than petroleum-based diesel (Krawczyk *et al.*, 1996; Korbitz *et al*., 1999). However, such small increases could be overcome by adjusting combustion temperature or engine timing (Krawczyk *et al.,* 1996).

In briefly, biodiesel appears to be good alternative to petroleum-based fuel and is being used in many countries, especially in environmentally sensitive areas. The most common way to produce biodiesel is by transesterification, which refers to a catalyzed chemical reaction involving vegetable oil and an alcohol to yield fatty acid alkyl esters and glycerol. Meanwhile, Triglyceride as the main component of vegetable oil, consists of the three long chain fatty acids esterifies to a glycerol backbone. When the triglyceride reacts with an alcohol (methanol), the three fatty acid chains are released from the glycerol skeleton and combine with methanol to yield fatty acid methyl esters (FAME). Glycerol is produced as a by-product. Methanol is most commonly used alcohol due low cost and in this process methanol chooses as the raw material.

2.2 Process Description

Nowadays, most of the biodiesel plant commercially operates based on the alkali-catalyzed. The process involves transesterification reaction in reactor, ester/glycerol separation process, biodiesel refining and glycerol refining. In addition, the raw material for the production of biodiesel are easy to obtain and renewable for example crude vegetable oil, waste cooking oil or animal fat or microalga can use as the raw material or feedstock. Figure 2.1 below shows the basic schematic for biodiesel production.

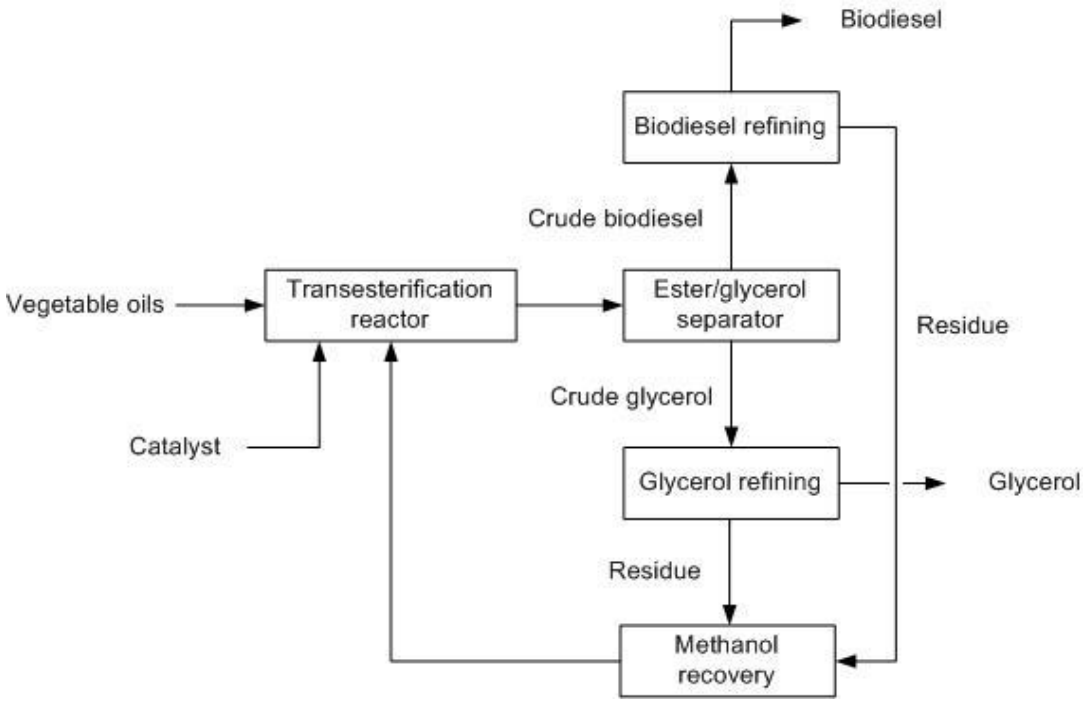


Figure 2.1: Basic schematic for Biodiesel production (Othman *et al.*, 2011)

2.2.1 Transesterification reaction

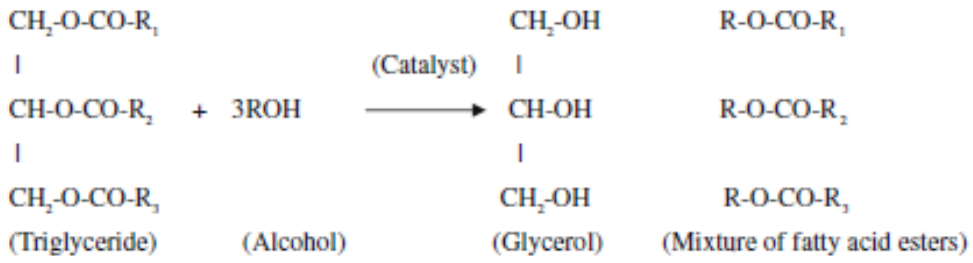


Figure 2.2: Biodiesel reaction. (Leung *et al*., 2010)

Figure 2.2 above shows the reaction for production of biodiesel through the transesterification reaction. In this reaction the long hydrocarbon chain sometimes called fatty acid chain which is R1, R2, and R3 react with alcohol (methanol) in presence of catalyst such as sodium hydroxide or potassium hydroxide to produce the mixture of ester and Glycerin or Glycerol. The ratio of methanol and oil is 3:1.

According to Leung et al. (2010), methanol is the preferred alcohol for producing biodiesel because of its low cost. Normally, there are five main types of chains in vegetable oils and animal oils: palmitic, stearic, oleic, linoleic, and linolenic. The common fatty acid and vegetable oil physicochemical properties are given in table 2.1

Fatty acid	Soybean	Cottonseed	Palm	Lard	Tallow	Coconut
Lauric	0,1	0,1	0,1	0,1	0,1	46,5
Myristic	0,1	0,7	1,0	1,4	2,8	19,2
Palmitic	10,2	20,1	42,8	23,6	23.3	9,8
Stearic	3,7	2,6	4,5	14,2	19,4	3,0
Oleic	22,8	19,2	40,5	44,2	42,4	6,9
Lonoleic	53,7	55,2	10,1	10,7	2,9	2,2
Linolenic	8.6	0,8	0,2	0,4	0,9	0,0

Table 2.1: Oil composition for various feedstocks. (F. Ma & M. A. Hanna., 1999)

Vegetable oils and fats may contain small amounts of water and free fatty acids (FFA). For an alkali-catalyzed transesterification, the alkali catalyst that is used will react with the FFA to form soap. The figure 2.3 shows the saponification reaction of the catalyst (sodium hydroxide) and the FFA, forming soap and water.

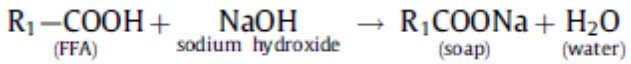


Figure 2.3: Saponification reaction. (Leung et al., 2010)

This reaction is undesirable because the soap lowers the yield of the biodiesel and inhibits the separation of the esters from the glycerol. In addition, it binds with the catalyst meaning that more catalyst will be needed and hence the process will involve a higher cost (Gerpen *et al*., 2004). Water, originated either from the oils and fats or formed during the saponification reaction, retards the transesterification reaction through the hydrolysis reaction. It can hydrolyze the triglycerides to diglycerides and forms more FFA. The typical hydrolysis reaction is shown in figure 2.4.

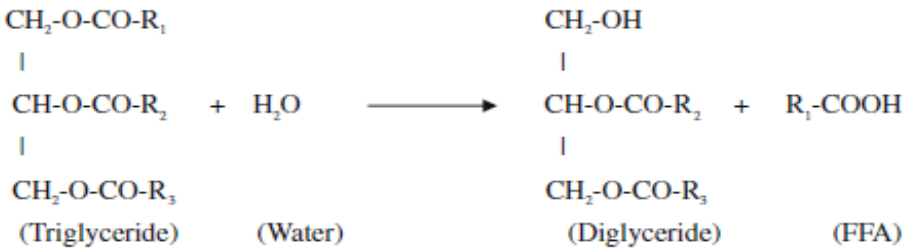


Figure 2.4: Hydrolysis reaction. [Leung *et al*., 2010]

However, the FFA can react with alcohol to form ester (biodiesel) by an acid-catalyzed esterification reaction. This reaction is very useful for handling oils or fats with high FFA, as figure 2.5 shown in the equation below:

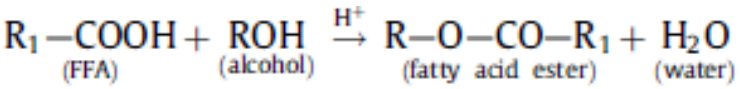


Figure 2.5: Acid-catalyzed esterification reaction. (Leung et al., 2010)

Normally, the catalyst for this reaction is concentrated sulphuric acid. Due to the slow reaction rate and the high methanol to oil molar ratio that is required, acid-catalyzed esterification has not gained as much attention as the alkali-catalyzed transesterification (Soriano *et al.*, 1999).

2.2.2 Ester/glycerol separation

The first step usually employed to recover biodiesel after transesterification reaction is separation of crude biodiesel from by-product, glycerol. The fast separation of biodiesel and glycerol is as a result of differences in their polarities and also significant difference in their densities. The density of biodiesel and glycerol are 0.88 gm/cc and 1.05 gm/cc or more respectively. The density of glycerol is dependent on the amount of water, catalyst and methanol present in it. This density difference is sufficient to employ simple gravity separation technique to separate biodiesel phase from glycerol phase (Gerpen *et al.*, 2004).

2.2.3 Biodiesel refining

The next step after separation process is biodiesel refining process. The process involves the water washing before go through the further refining process in order to produce quality of desired product. The objective for ester washing is to removal any soap that formed during transesterification reaction and also water reacts as the medium to neutralize the remaining catalyst. In addition, the residual methanol should be removed before washing steps in order to

prevent the addition of methanol to the wastewater effluent. There are some types of water that have difference function for the washing steps. In other hand, different types of water that used for washing have difference function for example the uses of warm water (49 to 60^{o}C) to prevents precipitation of saturated fatty acid esters and retards the formation of emulsions with the use of a gentle washing action meanwhile the uses of softened water (slightly acidic) eliminates calcium and magnesium contamination and neutralizes remaining base catalysts.

2.2.4 Side stream management

For biodiesel production there are basically three side streams that must be treated to optimize the stability of a biodiesel plant which are excess methanol, glycerol byproduct and wastewater. These side streams must be treated properly to minimize the environmental impact to the surroundings, especially methanol, which is highly flammable and toxic, and also maximize the profit from recovering glycerol which has higher value than biodiesel. Wastewater constitutes an operating cost for the plant, both of the water consumption of the water treatment cost of the plant.

Since glycerol is treat as by-product which recovered from the tranesterification reaction that contains some impurities of chemical such as residual alcohol, catalyst residue, oil and some ester. The by-product can be sold in order to increase plant profit due the widely use in industry such as food industry, pharmaceutical and personal care applications, botanical extracts, anti-freeze and chemical intermediate.

2.3 Technological option for biodiesel production

Today, most of the large scales of biodiesel plants were run base on alkali-catalyzed system due the high efficiency, low operating cost and less corrosive. But there are some disadvantages using that method which is the process is very sensitive to purity of reactant such as water and FFA content.

In addition, in order to reduce the cost of raw material, waste cooking oil used with high FFA. To ensure the good conversion acid catalyst provided as an excellent ways for feedstock with high FFA. The process gives quite high yield in esters. But, the process of reaction is slow which needed almost one day to accomplish. Despites the reaction can cause corrosion. Therefore, the method is less preferable in industry.

Other than that, there are attempts to use supercritical method (Kusdiana and Saka, 2001). By using that method, it shows that the FFA in the oils converted completely into fuel which the higher reaction rate experimentally. The method also can acceptable for wide variety feedstock. However, the process involves the high temperature and pressure will cause huge safety and expansive cost, thus is less preferable for the commercially.

Another similar approach to ultrasonic is by using hydrodynamic cavitation. An experimental works for biodiesel production with, the help of ultrasonic and hydrodynamic cavitation was done by Jianbing *et al*., (2009). Their result shows that the equilibrium reaction time was shortened in order:

Ultrasonic, hydrodynamic cavitation, mechanical stirring. $\longrightarrow$

and for energy consumption the efficiency is in order:

hydrodynamic cavitation, pulse ultrasonic, mechanical stirring. $\longrightarrow$

However, scale up of hydrodynamic cavitation had better opportunities than the ultrasonic reactor because of its easier generation and less sensitivity to the geometric details.

Other than using chemical-based catalyst, it is also reported that the use of enzyme such as lipase for biodiesel production (Shimada *et al.,* 1999). Using enzyme has the advantage that it has the possibility for regeneration and reuse, longer activation of the lipase and bigger thermal stability. Other than that, it protects solvents to be used in reaction and prevent enzyme particles getting together and ease of separation of product. However, the disadvantages are loss of initial activity due to volume of the oil molecule, the number of support enzyme is not uniform, and the cost is more expensive.

2.4 Supercritical methanol

2.4.1 Introduction

An alternative, catalyst-free method for transesterification uses supercritical methanol at high temperatures and pressures in a continuous process. In the supercritical state, the oil and methanol are in a single phase, and reaction occurs spontaneously and rapidly. The process can tolerate water in the feedstock, free fatty acids are converted to methyl esters instead of soap, so a wide variety of feedstocks can be used. Also the catalyst removal step is eliminated. High temperatures and pressures are required, but energy costs of production are similar or less than catalytic production routes.

During the last decade, the supercritical transesterification method for biodiesel production, a process carried out at temperatures of 280-400^{0}C and pressures in the range of 100-300 bar, has been extensively studied and proposed as an alternative to conventional base and acid catalyzed biodiesel production methods. Pioneered by Japanese researchers (Saka and Kusdiana, 2001), this method takes advantage of the homogeneous phase, which forms at supercritical conditions of the alcohol and triglycerides mixture, promoting fast transesterification reactions of triglycerides and simultaneous esterification of free fatty acids (FFA) without the need of a catalyst (Pinnarat and savage, 2008). Therefore, this method can process virtually any kind of raw triglyceride material, such as animal fats and waste vegetable oil, which are difficult or unfeasible to process through conventional biodiesel production methods. However, the high methanol to triglycerides molar ratios employed in almost all of the experimental studies to date, usually 42:1, remain a mayor nuisance for the development of the supercritical transesterification method at an industrial level, due to the expectedly high methanol pumping, preheating, and recycling costs.

2.4.2 Supercritical Method

Voll *et al.* (2010) remarked on the non-catalytic reaction, using alcohol under supercritical conditions at high temperatures and pressures. Thus the features of the supercritical method allows various resources such as swill oil and frying oil to be used as the feedstocks, thus

esters yield can be more than 96% (He *et al.,* 2007). Similarly, Van Kasteren and Nisworo (2007) reported that since waste cooking oil contains FFAs, adopting supercritical transesterification could offer huge advantages by erasing pre-treatment capital and running cost. Also, the presence of FFAs in feedstocks during transesterification with various supercritical alcohols does not have a significant effect on the yield (Wang *et al.,* 2007). Supercritical methanol is a high-density chemically labile vapor that cannot be compressed into the liquid state (80 bar, 240 ◦C). Supercritical methanol is miscible with oils and fats or FFAs (Davies *et al.,* 2005). It has been observed that supercritical methanol process for the transesterification of fats and oils can tolerate presence of higher FFAs (Imahara *et al.,* 2008).

Saka and Kusdiana (2001) stated the yield of esters produced by supercritical methanol method (SCM) is higher than that of the common method. Thus, the conversion of FFAs to methyl esters in supercritical process led to the increase yield. In common method, FFAs, is converted to saponified products by the alkaline catalyst. The authors recently found that these same FFAs are converted to methyl esters through the dehydration reaction during the supercritical treatment of methanol (Davies *et al.,* 2005). Further, Imahara *et al.* (2008) noted that non-catalytic supercritical methanol technologies are attractive processes in biodiesel production by overcoming problems such as incomplete conversion of oils/fats because of presence of FFAs.

Banerjee and Chakraborty (2009) noted that non-catalystic supercritical transesterification of WCO has provided biodiesel of high purity (99.8%) and almost pure glycerol (96.4%). It has been also reported that, supercritical methanol with a co-solvent process is superior to the conventional supercritical methanol method, thus providing more than 98wt% yield of methyl esters (Wang *et al.,* 2007). Additionally high conversions of 80–100% were recorded when the reaction was conducted in supercritical methanol and ethanol. However, reaction catalyzed by an enzyme in supercritical carbon dioxide provided low conversions of 27–30% (Madras *et al.,* 2004).

2.4.3 Flowsheet of supercritical methanol

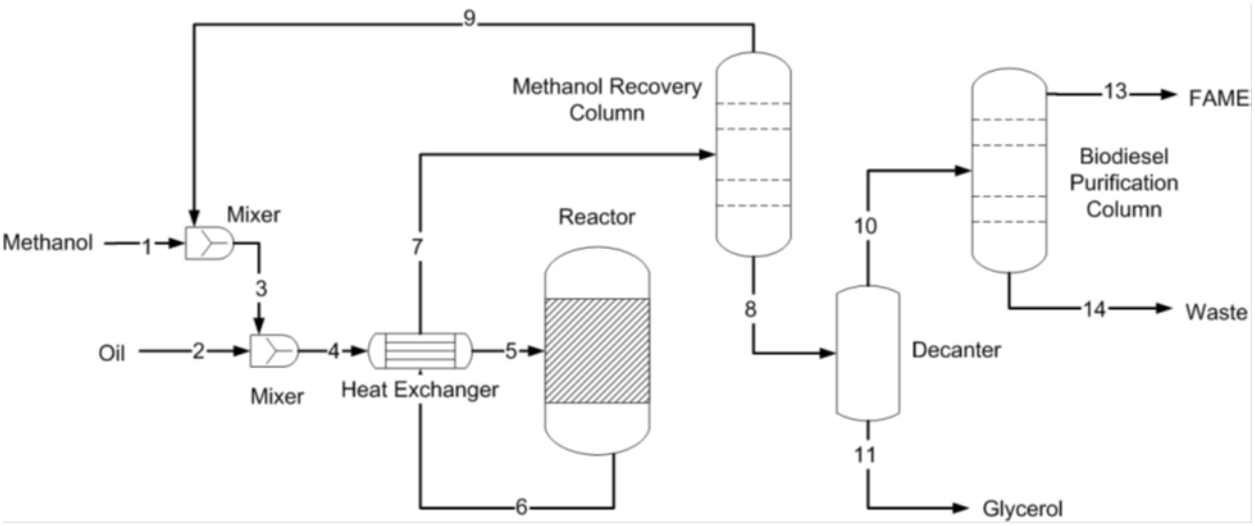


Figure 2.6: Flowsheet for supercritical methanol (Lim *et al.*, 2009)

The flowsheet of supercritical methanol configuration is shown in figure 2.6 base on the research Lim *et al.* (2009). In this work, the reaction condition with 42:1 methanol to oil molar ratio, temperature at 350^{o}C and pressure at 430 bar are used. According to Lim *et al*. (2009), at this condition, the reaction takes only four minutes with the yield of 95%. Because of the high temperature of the reactor output stream, the heat is utilized to preheat the reactor input stream using heat exchanger while maintaining the product below 250^{o}C. The reaction product then enters the methanol recovery distillation column with 12 theoretical stages and the reflux ratio of 0.5. Nearly 99.6% of the excess methanol can be recovered with the purity nearly 99.9%. This recycled methanol is mixed with the fresh methanol feed of 114 kg/hr before being fed again, together with oil, to the reactor.

The bottom stream of the column is then cooled down before being sent to a decanter. Based on the component density, the upper part contains 94.7% biodiesel and the rest is unreacted oil and other impurities. The bottom stream contains over 92% of glycerol and the rest is mostly methanol. As the purity of glycerol meets the commercial standard, no further purification step is needed. The biodiesel rich stream still needs to undergo further purification.

The stream is fed to a biodiesel purification column using eight theoretical stages with the reflux ratio of 0.05 and under vacuum. The biodiesel purity at the distillate stream achieves the product specifications of more than 99.6wt%.

2.5 Environmental Assessment

An environmental impact assessment is an assessment of the possible positive or negative impact that a proposed project may have on the environment, together consisting of the environmental, social and economic aspects. The purpose of the assessment is to ensure that decision makers consider the ensuing environmental impacts when deciding whether to proceed with a project. According to Young and Cabezas (1999), they have introduced a so-called waste reduction (WAR) algorithm for assessing environmental impact of a chemical process design. The concept of potential environment impact (PEI) in the WAR algorithm is based on the conventional mass and energy balance conducted at the manufacturing level. PEI is a relative measure of the potential for a chemical to have an adverse effect on human health and environment. The result of the PEI balance is an impact index that provides quantitative measure of the impact of the waste generated in the process.

Apart from that, there are some advantages to use this algorithm which is simple to use and easy to find the parameters. Furthermore, it is inherently flexible, which allows the user to emphasize or de-emphasize the individual impact categories in the calculation of the pollution indices to address their specific needs. Because of its suitability in assessing environmental performance at the design stage, the WAR algorithm has been integrated into several process simulators such as ChemCAD, Integrated Computer Aided System (ICAS) and AspenTech.

In addition, establishment of standardized and commonly accepted environmental methodology has a long way to go. There are still efforts to identify or improve ways to measure environmental performance of a system. None of the fore mentioned methodologies have become a standard or approved method to assess environmental effects of a process design. Different organizations or individuals may use different methods based on their preferences. The adoption of a particular indicator is significantly important, especially in the initial stages of process design, so that the indicator presents a direct correlation among flows and impacts and

reduces the requirement of complex models (Kasteren *et al.*, 2007). WAR algorithm is adopted to assess the environmental performance of a process design. The reason is because of its ability to describe the environmental impact of the input-output material and energy stream in a simple approach (Othman *et al.*, 2011). Moreover, it uses less extensive data which can be found in open literature and could greatly facilitate design comparison to modified or new processes. The equation below is the formula for the Waste Reduction (WAR) algorithm.

2.5.1 Potential Environmental Impact Theory

Potential environmental impact (PEI) in WAR algorithm is defined as the effect that the specified quantity of material and energy would have on the environment when they are exposed to the environment (Young & Cabezas, 1999).
At steady state, PEI balance may be expressed as:

$$0 = I_{in}^{(cp)} + I_{in}^{(ep)} - I_{out}^{(cp)} - I_{out}^{(ep)} - I_{we}^{(cp)} - I_{we}^{(ep)} + I^{t}_{gen} \quad (2.1)$$

Where $I_{in}^{(cp)}$ and $I_{out}^{(cp)}$ are the mass input and output rates of PEI to the chemical process, $I_{in}^{(ep)}$ and $I_{out}^{(ep)}$ are the input and output rate of PEI to the energy generation process, $I_{we}^{(cp)}$ and $I_{we}^{(ep)}$ are the outputs of PEI associated with waste energy lost from the chemical process and the energy generation process which will be neglected due to the minor impact they give. I^{t}_{gen} is the rate of generation of PEI inside the system.

The equation is then reduced to:

$$0 = I_{in}^{(cp)} + I_{in}^{(ep)} - I_{out}^{(cp)} - I_{out}^{(ep)} + I^{t}_{gen} \quad (2.2)$$

PEI generation index, I^{t}_{gen} can be calculated by the equation below:

$$I^{t}_{gen} = I_{out}^{(t)} - I_{in}^{(t)} \quad (2.3)$$

$$I_{in\,(t)} = \sum_i^{EnvCat} \alpha_i I^{(t)}_{i,in} = \sum_i^{EnvCat} a_i \sum_j^{Streams} M_{j,in} \sum_k^{Comps} x_{kj}\, \varphi^s ki \quad (2.4)$$

Where α_i is the weighting factor associated with PEI category I, $I^{(t)}_{i,in}$ is the PEI input index for category i, $M_{j,in}$ is the mass flow rate of input stream j, x_{kj} is the mass fraction of component kin stream j, and $\varphi^s ki$ is the specific PEI of component k associated with environmental impact category i.

$$I_{out\,(t)} = \sum_i^{EnvCat} \alpha_i I^{(t)}_{i,out} = \sum_i^{EnvCat} a_i \sum_j^{Streams} M_{j,out} \sum_k^{Comps} x_{kj}\, \varphi^s ki \quad (2.5)$$

Where $I^{(t)}_{i,out}$ is the PEI output index for category I and $M_{j,out}$ is the mass flow rate of the product output stream j.

2.5.2 Potential Environmental Impact Indexes

Two types of environmental impact indexes are used in analyzing the environmental friendliness of chemical process which is: PEI output indexes and PEI generation indexes (Young *et al.*, 1999).

The output indexes can be in the terms of rate PEI/h or on production basis, PEI/kg. The algorithm used earlier is on a rate basis (PEI/h). In the production basis form (PEI/kg), the equations below are used:

$$\hat{I}^t_{out} = \frac{I^t out}{\sum_P^{ProdStreams} P_p} \quad (2.6)$$

$$\hat{I}^t_{gen} = \frac{I^t gen}{\sum_P^{ProdStreams} P_p} \quad (2.7)$$

Where $\hat{I}^t_{out}$ is the PEI output index, $\hat{I}^t_{gen}$ is the PEI generation index, and P_p is the mass flow rate of the product streams.

$I^t out, \hat{I}^t_{out,}$ $I^t gen_,$ $\hat{I}^t_{gen,}$ are used to compare the environmental friendliness of the process design. $I^t out$is useful in identifying the appropriate site for a plant where a plant with low $I^t out$must be located in ecologically sensitive area. $\hat{I}^t_{out,}$ measures the efficiency of material utilization by a specific process per unit mass of products where it is decreases with the reduction of $I^t out$or when the production rate is increased. Thus, improved the material utilization efficiency through process modification decreased the output PEI/kg of product. $\hat{I}^t_{gen}$, is used for comparing processes and products based on the amount of new PEI generated in product manufacturing (Othman *et al*., 2011). The environmentally desirable design is those with the lowest PEI index values.

2.5.3 Specific PEI of Chemical Components

In implementing the WAR algorithm, the specific PEI of each chemical over certain impact category, $\varphi^s ki$, must be determined. Eight environmental impacts are used in this study which can be categorized into two categories:

Global atmospheric:

i. Global warming potential (GWP)
ii. Ozone depletion potential (ODP)
iii. Acidification potential (AP)
iv. Photochemical oxidation potential (PCOP)

Local toxilogical:

i. Human toxicity potential by investigation (HTPI)
ii. Human toxicity potential by inhalation/dermal exposure (HTPE)
iii. Aquatic toxicity potential (ATP)
iv. Terrestrial toxicity potential (TTP)

The value of specific PEI of each chemical components involved are then exported the Microsoft Excel together with the data get from simulation process such as the stream flowrates

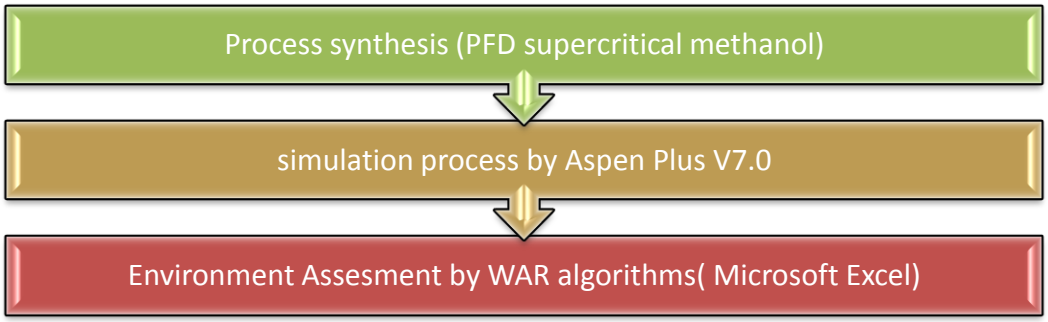
and compositions, utilities, and operating conditions of pressure and temperature. Mass and energy balances are then performed using the equations above. Results obtained are then analyzed. Those with lower PEI value are preferable (Othman *et al.*, 2011).

CHAPTER 3

RESEARCH METHODOLOGY

3.1 Introduction

In this paper, the overall process can be divided into three stages which is show at the schematic process below.



3.2 Process synthesis

In this work, the case is model using supercritical methanol. Basic steps to process modeling and simulation using process simulators include defining chemical components, selecting thermodynamic model and method, designing process flowsheet by choosing proper operating units, determining plant capacity and setting up input parameters based on study of Othman *et al.* (2011) and Lim *et.al* (2009).

3.3 Process Simulation

Process simulation was carried out to assess the feasibilities of commercial process from the proposed process. From the simulation process, mass, component and energy balances of each unit operation as well as the operating conditions were obtained which will further used in

environmental assessment. In this study, the process simulation is using Aspen Plus 7.0 and all the parameter involves based on research done by Othman *et al*. (2011)

3.4 Chemical component

The raw material that used is rapeseed oil as a raw material. The table 2.2 below shows the chemical compound that involves in simulation supercritical process.

Compound	Component name	Component ID	formula
TG	Triolein	TRIOLEIN	$C_{57}H_{104}O_6$
Glycerol	Glycerol	GLYCE-01	$C_3H_8O_3$
Methanol	Methanol	METHA-01	CH_4O
Methyl oleate	Methyl oleate	METHY-01	$C_{19}H_{36}O_2$

Table 2.2: Compound defined in Aspen Plus

3.5 Thermodynamic model and method

In the production of biodiesel, methanol and glycerol are highly polar component. Therefore, NRTL and UNIQUAC are used as thermodynamic method in order to predict the coefficient of the component in a liquid phase (Zhang *et al.*, 2003). In this simulation NTRL is used as the main of thermodynamic method. In addition, Predictive Soave-Redlich-Kwong (PSRK) thermodynamic properties are used for designing distillation column, decanter and reactor due involves pressure which is more than 10 bar (Othman *et al.* 2011). Most of the compound properties are available in Aspen Plus component library. Even though, some of them have to estimate. For example, even Triolein in chemical database, some of the properties such as molecular structure need to inserted to run the simulation process properly.

3.6 Process flowsheet design

Then, the modeling process is continuing by designing the process flowsheet. In this case, the simulate capacity is 8000 ton/yr with oil feed input of 1050 kg/hr and 114 kg/h of methanol. The flowsheet of biodiesel production via supercritical shows in figure 3.1 and the summary for specification of operation shows in table 2.3.

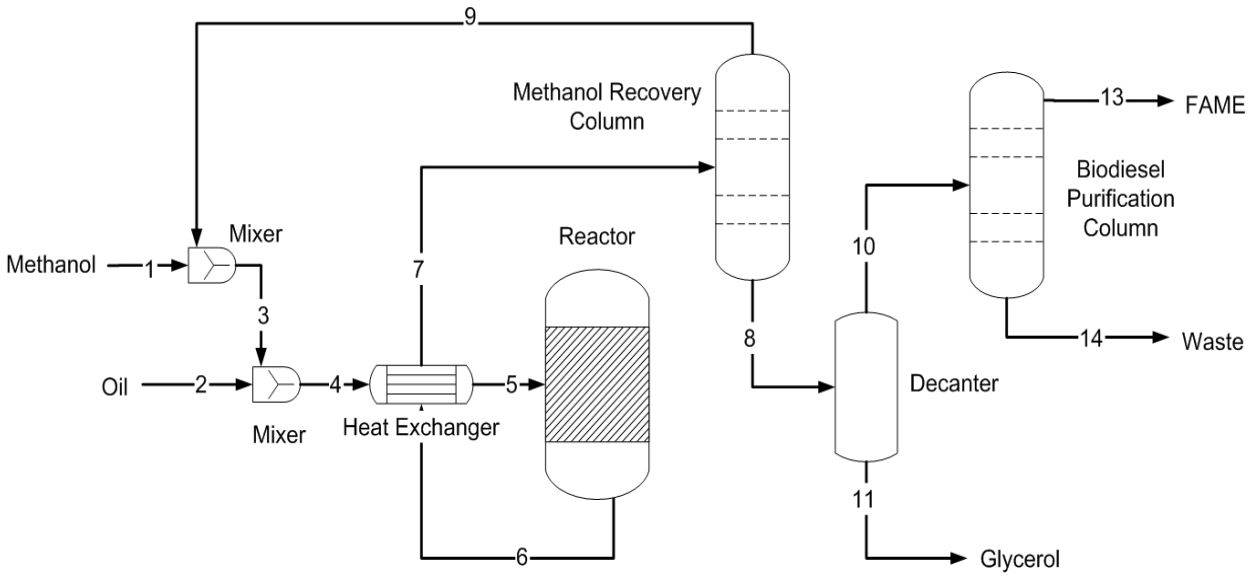


Figure 3.1: process flowsheet of supercritical methanol (Lim *et al.*, 2009)

Operating specification	Case study : supercritical methanol
Transesterification reactor	
Catalysts	N/A
Reactors types	CSTR
Temperature, ^{0}C	350
Pressure, bar	430
Alcohol: oil molar ratio	42:1
Residence time, min	4
Conversion, %	95
Methanol recovery column	
Reflux ratio, mass	0.5
Number of stages	12
Distillate/bottom temperature, ^{0}C	64.5/158.3
Condenser/Reboiler pressure, kPa	101.3/105.3
Recovery, %	99.6
Distillate flowrate, kg/hr	1487.7
Distillate purity, wt%	99.9
Biodiesel purification column	
Reflux ratio, mass	0.05
Number of stages	8
Distillate/bottom temperature, ^{0}C	49.8/356.4
Recovery, %	99.6
Distillate flowrate, kg/hr	1002.0
Distillate purity, w%	>99.7

Table 2.3: operating specification of biodiesel via supercritical methanol (Othman *et al.,* 2011)

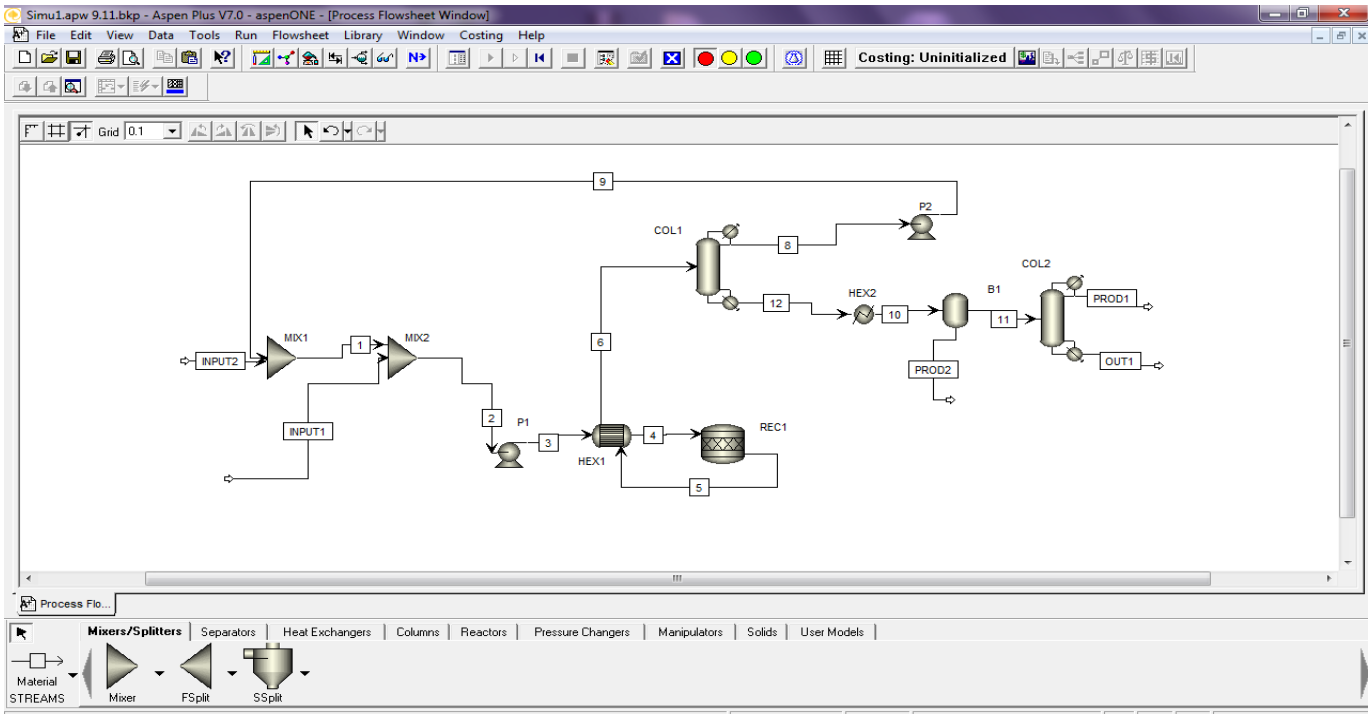


Figure 3.2: Process flowsheet of supercritical methanol in Aspen plus

Results from simulation provided the mass balances and operating conditions for the equipment where the information was exported to the spreadsheet for environmental assessment of the process using WAR Algorithm method.

3.7 Environment Assessment

3.7.1 WAR Algorithm

In WAR algorithm method, the component-specific potential environment impact (PEI) parameters were keys in to the spreadsheet together with the data from the process simulation in Aspen Plus v7.0.

3.7.2 Data from Process Simulation

The data were specified based on the aspen results of input and product streams, and non-product or waste steam. In this process, input streams were methanol (INPUT1 stream) and

Triolein (INPUT2 stream). Product streams were glycerol (PROD2 stream) and biodiesel (PROD1 stream). Non-product or waste stream went to Triolein output (OUT1 stream).

Parameters defined included the operating temperature and pressure of each streams involved, and the mole and mass flowrates and composition of each component present in the stream.

CHAPTER 4

RESULT AND DISCUSSION

4.1 Introduction

In this chapter, results of biodiesel process from simulation of Aspen Plus v7.0 and environmental assessment are presented. Apart from that, an environmental assessment results done by Eleyana (2012) on the heterogeneous catalysis of biodiesel process are presented and further discussed in the environmental assessment by comparing the result of environmental performance in this paper.

4. 2 Simulation Result

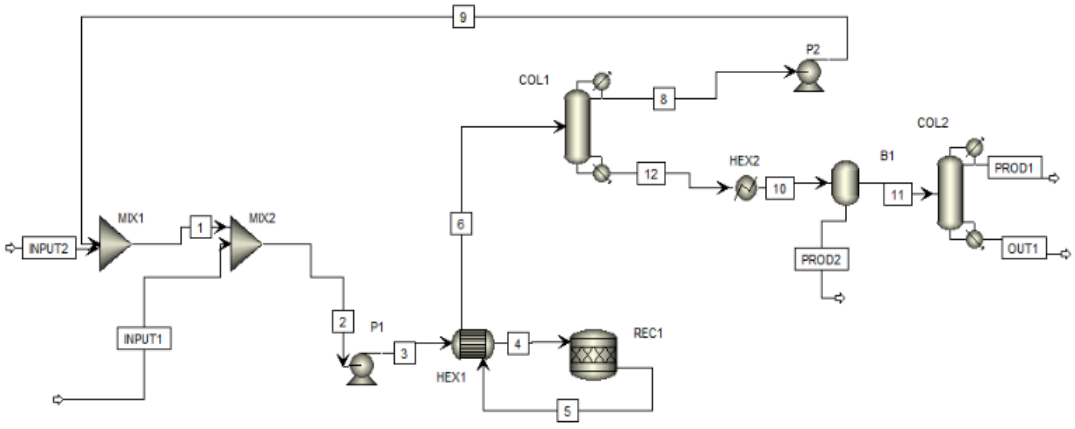


Figure 4.1: Flowsheet of supercritical methanol defined in Aspen Plus

PRODCUTION OF BIODIESEL VIA SUPERCRITICAL METHANOL																	
Stream ID		1	2	3	4	5	6	7	8	9	10	11	INPUT1	INPUT2	OUT1	PROD1	PROD2
Temperatura	C	48.5	44	96.5	250	350	232.5	158.3	64.5	64.5	40	30	30	30	356.4	49.8	30
Pressure	bar	1	1	430	430	430	430	1.053	1.013	1	1.013	1	0	1	0.15	0.1	1
Vapor Frac		0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0
Mole Flow	kmol/hr	49.888	51.173	51.173	51.173	51.173	51.173	4.744	46.43	46.43	4.744	3.54	1.186	3.558	0.073	3.467	1.204
Mass Flow	kg/hr	1601.709	2651.709	2651.709	2651.709	2651.709	2651.71	1164	1487.709	1487.71	1164	1058.58	1050	114	56.58	1002	105.42
Volume Flow	cum/hr	2.095	4.177	6.322	7.648	7.158	5.531	1.959	2.628	2.628	1.823	1.242	1.159	0.145	0.195	1.549	0.085
Enthalpy	MMkcal/hr	-2.819	-3.42	-3.238	-2.967	-2.783	-2.783	-0.724	-2.616	2.616	-0.81	-0.619	-0.601	-0.202	-0.02	-0.593	-0.18
Mass Flow	kg/hr																
TRIOLEIN		0	1050	1050	1050	52.5	52.5	52.5	0	0	52.5	52.458	1050	0	52.44	0.01	0.042
METHA-01		1601.709	1601.709	1601.709	1601.709	1493.418	1493.42	5.709	1487.709	1487.71	5.709	2.784	0	114	0	2.784	2.925
GLYE-01		0	0	0	0	103.749	103.749	103.749	0	0	103.749	1.296	0	0	0	1.296	102.453
METHY-01		0	0	0	0	1002.042	1002.04	1002.042	0	0	1002.04	1002.04	0	0	4.132	997.91	0
Mass Frac																	
TRIOLEIN		0	0.396	0.396	0.396	0.02	0.02	0.045	0	0	0.045	0.05	1	0	0.927	0	0
METHA-01		1	0.604	0.604	0.604	0.563	0.563	0.0005	1	1	0.005	0.003	0	1	0	0.003	0.028
GLYE-01		0	0	0	0	0.039	0.039	0.089	0	0	0.089	0.001	0	0	0	0.001	0.972
METHY-01		0	0	0	0	0.378	0.378	0.861	0	0	0.861	0.947	0	0	0.073	0.996	0

Table 2.4: summary result of stream table for production of biodiesel via supercritical methanol

4.3 Discussion

4.3.1 Reactor, REACT1 (transesterification)

The reaction was carried out at a 42:1 molar ratio of methanol to oil, temperature at 350^0C and pressure at 430 bar. Nearly 99.6% of the excess methanol is mixed with the recovered with the purity nearly 99.9%. This recycled methanol is mixed with the fresh methanol feed of 114 kg/hr before being feed again, together with oil, to the CSTR Reactor (REC1). At the stream 4, the input enters which are 1050kg/h (39.6%) of TG and 1601.709kg/h (60.4%) of methanol respectively. Meanwhile, at the stream 5, output stream contains 52.5kg/h (2%) of TG, 1493.418kg/h (56.3%) of methanol, 103.749kg/h (3.9%) of glycerol and 1002.04kg/h (0.378%) of FAME. At stream 5, the temperature and pressure are 350^0C and 430 bar which is same condition for the chemical reaction in reactor.

4.3.2 Distillation column, COL1 (Methanol Recovery)

In COL1, 12 theoretical stages, 0.5 of reflux ratio and 1379.41801kg/h of distillate rate are set as operation condition. At stream 6, the temperature is 232.5^{0}C and the pressure is 430 bar. In addition, for the composition of component that fed into stream 6 are 52.5kg/h (2%) of TG, 1493.42kg/h (56.3%) of methanol, 103.749kg/h (3.9%) of glycerol and 1002.042kg/h (37.8%) of FAME respectively. The total methanol fed to the column was recovered in the distillate (stream 8) which is 1487.709kg/hr (>99.9%) of methanol. Meanwhile, for bottom stream (stream 7), the temperature and pressure are 158.3^{0}C and 1.053 bar respectively. The composition of component contains at bottom stream are 52.5kg/h (4.5%) of TG, 5.709kg/h (0.5%) of methanol, 103.749kg/h (8.9%) of glycerol and 1002.042kg/h (86.1%) of FAME. Next, all of bottom component are send to decanter (DEC1) in order to separate glycerol (PROD2).

4.3.3 Decanter (DEC1)

In order to purify the production of FAME, the component of stream 7 will fed to decanter to separate the glycerol. The method that used for separation process at decanter is based on density difference. This density difference is sufficient enough for the use of simple gravity separation techniques for the two phases. Since glycerol is denser than FAME and other impurities, glycerol will go bottom stream (PROD2) of decanter. But before fed to the decanter, the component at stream 7 will through the heat exchanger (HEX2) to lowering the temperature form 158.3^{0}C to 40^{0}C. In addition, the compositions of component at stream 10 are 52.5kg/h (4.5%) of TG, 5.709kg/h (0.5%) of methanol, 103.749kg/h (8.9%) of glycerol and 1002.042kg/h (86.1%) of FAME. Meanwhile, at the stream PROD2 the composition of glycerol is about 102.453kg/h (97.2%) of glycerol.

4.3.4 Distillation Column, COL2 (FAME purification)

In Distillation column (COL2), 8 theoretical stages, 0.05 of reflux ratio and 1002.04081 kg/h of distillate rate are set as operation condition. At the stream 11, the temperature and pressure are 30^{0}C and 1 bar respectively. Meanwhile, the compositions of component are 53.458

kg/h (5%) of TG, 2.784kg/h (0.3%) methanol, 1.296kg/h (1%) of glycerol and 1002.042 kg/h (94.7%) of FAME. For the stream PROD1, the temperature is 49.8^{0}C and the pressure is 0.1 bar. The total of FAME composition distillate at the top of column (stream PROD1) is about 997.91kg/h (99.6%). Other than that, there are some of other composition of component distillate at the top column which is 0.01kg/h (0.0%) of TG, 2.784kg/h (0.3%) of methanol and 1.296 kg/h 0.1%) of glycerol. Next, at stream OUT1 the temperature and pressure are 356^{0}C and 0.15 bar respectively. The composition of component at that stream have only two compound which are 52.449 kg/h (92.7%) of TG and 4.132(7.3%) of FAME that treat as waste.

4.4 Environment Assessment

Basically, environmental assessment performance is discussed contain element such as the total rate output (TRO), total rate output/product (TOP), total rate generation (TRG), and total rate generation/product (TGP). In this sub result, TRO of each environmental impact categories are continuous to discussed by comparing the results with environmental assessment results of Heterogeneous catalysis of biodiesel process. WAR algorithm is applied there as a comparison tool in selecting environmentally first stage design option.

4.4.1 PEI result

Indicator	input stream	Output	stream	With	product	stream			Without	product	stream		
		product stream	Non-prod stream	Output/ product	TRO	TOP	TRG	TGP	Output/ product	TRO	TOP	TRG	TGP
HTPI	157.6036866	72.1306	0	0.06513	72.1306	0.065134	-85.4731	-0.07718	0	0	0	-157.604	-0.14232
HTPE	217.1428571	21.2024	0	0.01915	21.20242	0.019146	-195.94	-0.17693	0	0	0	-217.143	-0.19608
ATP	0.452772544	206.553	0	0.18652	206.5532	0.186517	206.1004	0.186109	0	0	0	-0.45277	-0.00041
TTP	157.6036866	72.1306	0	0.06513	72.1306	0.065134	-85.4731	-0.07718	0	0	0	-157.604	-0.14232
GWP	0	0	0	0	0	0	0	0	0	0	0	0	0
PCOP	81.05202312	1290.66	5.32408	1.17028	1295.989	1.170278	1214.937	1.097088	0.004808	5.32408	0.004808	-75.7279	-0.06838
AP	0	0	0	0	0	0	0	0	0	0	0	0	0
ODP	0	0	0	0	0	0	0	0	0	0	0	0	0
Total	613.8550261	1662.68	5.32408	1.50621	1668.006	1.506209	1054.151	0.951898	0.004808	5.32408	0.004808	-608.531	-0.5495

Table 2.5: Overall PEI results of supercritical process.

Indicator	Input stream	Output stream			With product stream					Without product stream			
		Product stream	Non-prod. stream	Output/ prod.	TRO	TOP	TRG	TGP	Output/ prod.	TRO	TOP	TRG	TGP
HTPI	141.9891	60.76178	2.55E-07	0.05795	60.76178	0.05795	-81.2273	-0.07746	2.43E-10	2.55E-07	2.43E-10	-141.989	-0.13541
HTPE	195.62943	9.37122	3.93E-08	0.00894	9.37122	0.00894	-186.258	-0.17762	3.75E-11	3.93E-08	3.75E-11	-195.629	-0.18656
ATP	0.4079141	196.4048	8.23E-07	0.1873	196.4048	0.1873	195.9969	0.18691	7.85E-10	8.23E-07	7.85E-10	-0.40791	-0.00039
TTP	141.9891	60.76178	2.55E-07	0.05795	60.76178	0.05795	-81.2273	-0.07746	2.43E-10	2.55E-07	2.43E-10	-141.989	-0.13541
GWP	0	0	0	0	0	0	0	0	0	0	0	0	0
PCOP	73.021795	1224.833	0.194559	1.16825	1225.027	1.16825	1152.006	1.09861	0.000186	0.194559	0.000186	-72.8272	-0.06945
AP	0	0	0	0	0	0	0	0	0	0	0	0	0
ODP	0	0	0	0	0	0	0	0	0	0	0	0	0
Total	553.03735	1552.132	0.19456	1.48037	1552.327	1.48037	999.2896	0.95297	0.000186	0.19456	0.000186	-552.843	-0.52722

Table 2.6: Overall PEI results of heterogeneous process [Eleyana, 2012]

Environmental Indicator	Heterogeneous Catalysis		Supercritical methanol	
	With product	Without product	With product	Without product
TRO	1552.33	0.19	1668.01	5.32
TOP	1.48	0.00	1.51	0.00
TRG	999.29	-552.84	1051.45	-608.53
TGP	0.95	-0.53	0.95	-0.55

Table 2.7: Environmental indicator total results

The overall PEI result of heterogeneous catalysis and supercritical methanol are shown in table 2.7. The parameters of environment indicator are TRO, TOP, TRG and TGP for with product stream and without product stream.

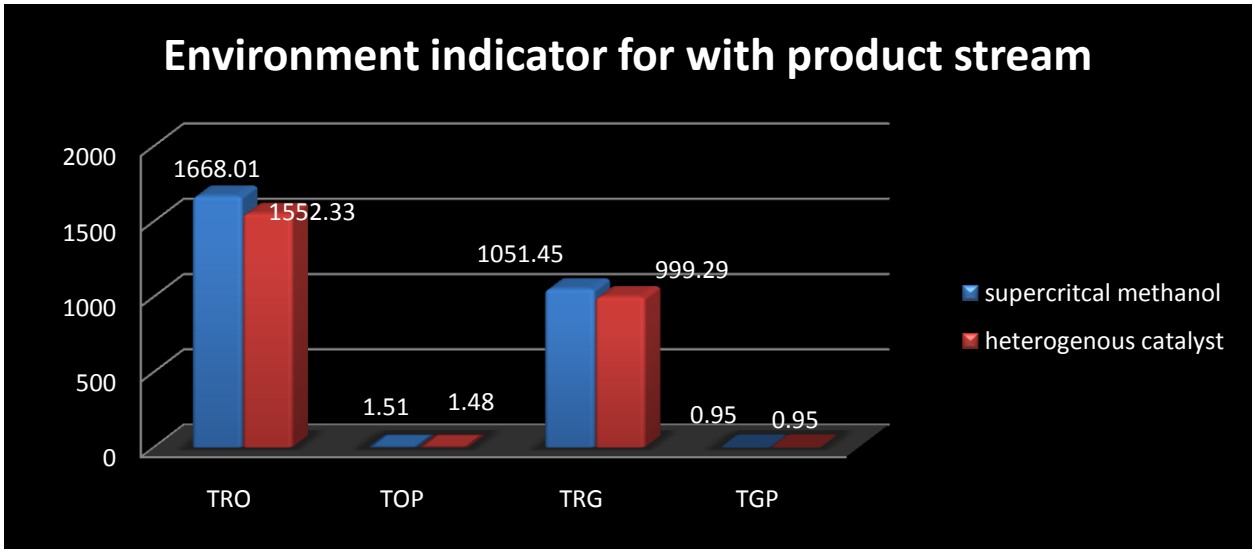


Figure 4.2: Environment indicator (with product stream)

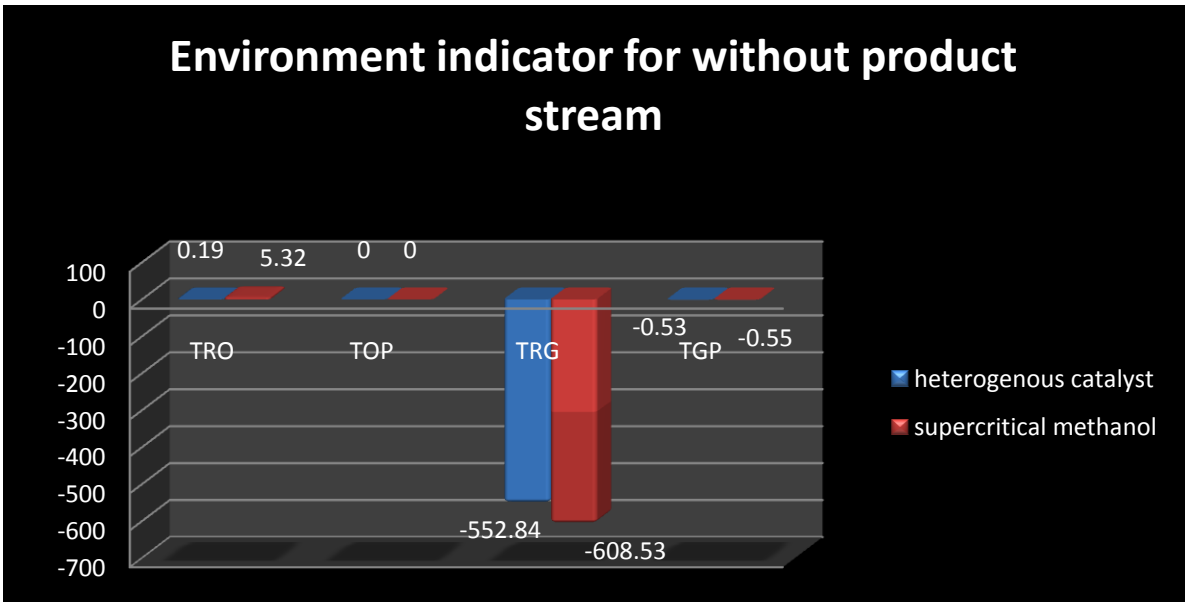


Figure 4.3: Environment indicator (without product stream)

The values obtained can be used as an index to compare several design options. Based on the PEI result the Total rate output (TRO) value is used to select a process design with the least environmental impact to be built in ecological sensitive area. According to figure 4.2 and figure 4.3, total TRO outputs are 1668.01 (product) and 5.32 (waste). The values are higher than heterogeneous process which is 1552.33 (product) and 0.19 (waste). Thus, heterogeneous catalysis is preferable due to the lower TRO result.

In addition, for the Total rate output/product (TOP) seem like the heterogeneous process less the Total rate output/product (TOP) compare to the supercritical process which is 1.48 and 1.51 respectively. Other than that, Total rate output/product (TOP) actually measures the efficiency of material utilization by a specific process per unit mass of products. TOP value decreases when the mass rate of PEI and TRO is reduced and the production rate is increased. Thus, improving material utilization efficiency through process modification tends to lower the PEI output per unit mass of products. PEI results show that heterogeneous offer a lower TOP value which is preferable in process selection.

Besides that, for the Total rate generation (TRG) is a result that is affected by the selection of process operating conditions. According to the result obtain, the TRG for supercritical process is higher compare to the heterogeneous process which both produce product rate about 1051.45 and 999.29 respectively. Meanwhile, for the waste stream supercritical produce the lower rate of TRG which is about -608.53 and heterogeneous produces at waste stream about -552.84. Commonly, TRG is used as an indicator in comparing process based on how fast they generate impact. Process with lower TRG value is preferable as the process tends to generate the environmental impact slower than process with higher TRG. Thus, heterogeneous process is preferable.

Total rate generation/product (TGP) is used for comparing processes and products based on the amount of new potential environmental impact generated in product manufacturing. Based on the result of PEI, the data show that the rate produce at product stream both is same 0.95. The supercritical process produce less rate if TGP rather that heterogeneous process which is -0.55 and -0.53 respectively. Thus, supercritical process which results in lower TGP value is much desirable and preferable in the production of biodiesel.

4.4.2 Total Rate Output (TRO) of production of biodiesel via supercritical

TRO information from the WAR algorithm is used to discuss the PEI for all the environmental categories which are divided into two categorize which is: with product (all output streams) and without product (waste product). As a mention before in methodology, each category is defined based on eight different environmental impacts which are HTPI, HTPE, ATP, TTP, GWP, PCOP, AP, and ODP.

4.4.2.1 TRO for stream PROD1 and stream PROD2

Bar chart is plotted based on the total rate output, TRO of each impact categories.

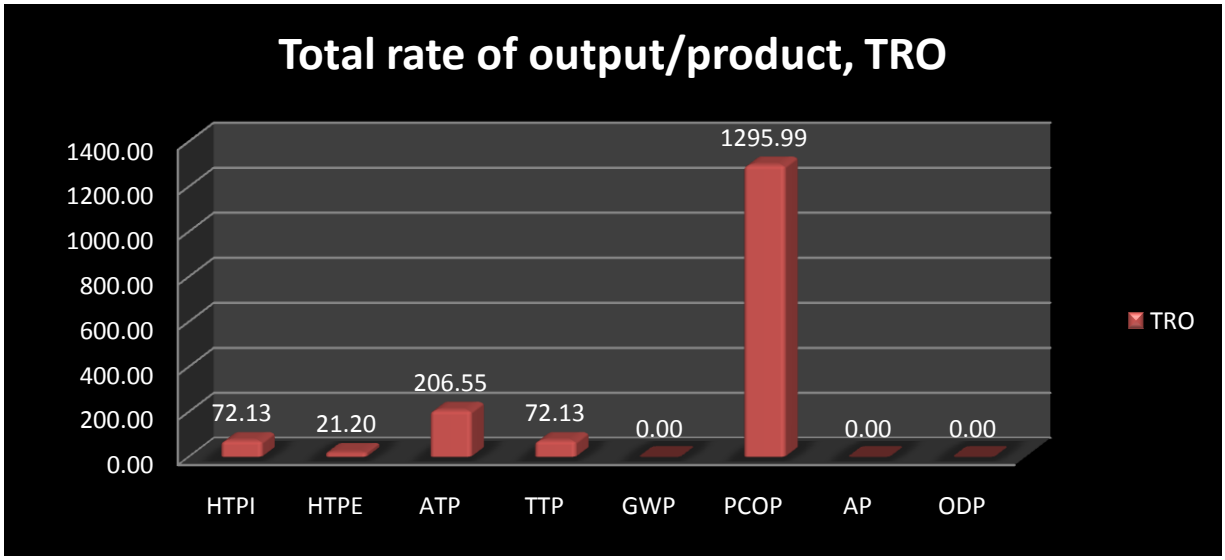


Figure 4.4: Total rate outputs of environmental impact categories

Based on the bar chart plotted, it indicates that PCOP give the highest TRO value among the environmental categories which is 12295.99 since the product is mostly covered by FAME. It is followed by ATP with value of 206.55 with methanol and glycerol existence in the product stream. HTPI and TTP show the same value which is 72.13 while HTPE show the lowest TRO value of 21.20. GWP, AP and ODP show zero value of TRO.

WAR algorithm method is useful to perform the impact categories where from the bar chart above, we can identify some impact categories that may be highlighted. TRO of PCOP shows the highest value which allows the user to focus on reducing the effect of photochemical oxidation for example smog formation. Toxicity control upon the process may be focus as well since the PEI results showed the existence of toxicity potential to aquatic and terrestrial, and toxicity potential to human either by ingestion or inhalation/dermal exposure.

4.2.2.2 TRO for waste stream OUT1

Bar chart is plotted based on the total rate output, TRO of each impact categories.

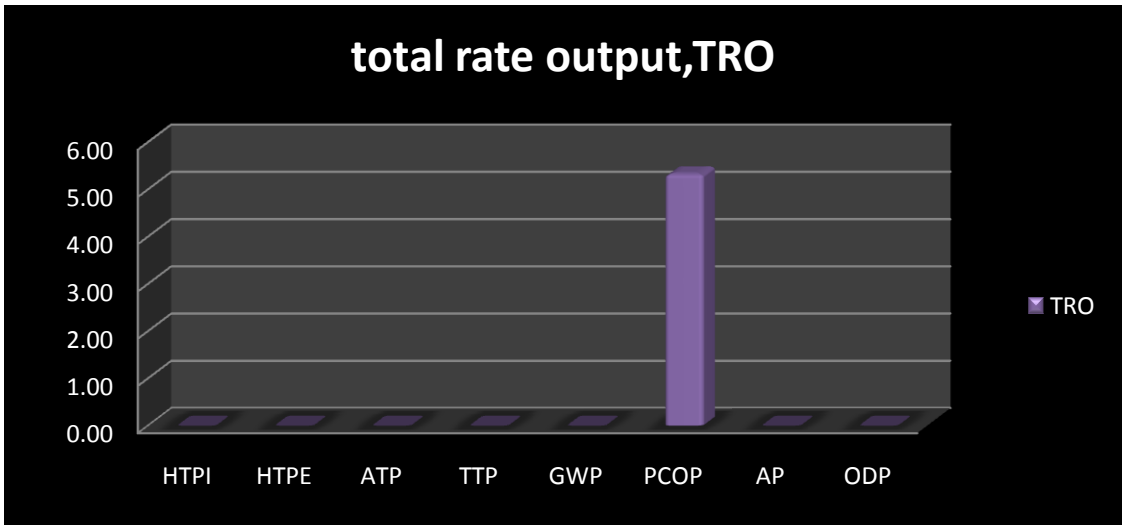


Figure 4.5: Total rate outputs of environmental impact categories (without product)

Bar chart above shows the TRO value of PCOP environmental impact only which is 5.32. Other categories show zero TRO output in the case where only waste stream is considered. PCOP value dominates the effect to the environment compared to others due to the presence of little amount of FAME in the non-product output stream. FAME leads to the result due to the high value of its PCOP specific PEI. WAR algorithm results act as retrofitting tool which allows users to identify spots or points in the design for further improvement. In this case, improvement on FAME purification can be made to reduce the amount of FAME in the non-product stream thus reducing the smog potential due to the effect of waste.

4.5 Simulation Difficulties

Simulation difficulties are about the problem occurs during the simulation process. There are several problems that identify will cause that process and ways to run the simulation process become hard to solve. In this paper, the problem that student facing are:

1. Not really well and clear understands the concepts of thermodynamic for the chemical reaction involves. The lack of knowledge regarding thermodynamic properties will cause the simulation result has much error to solve.
2. In the process of simulation, student lack of skill and knowledge in Aspen plus. For example, student tends to choose wrong equipment to develop process flow diagram.
3. Aspen plus is not stable and crash by suddenly terminate during the simulation process. The work in progress become corrupted and error. Therefore, the process of simulation needs to redo again to achieve the objective of study.
4. Some of chemical structure is not in database of Aspen Plus and need to import from the internet for example Triolein.
5. Student not really understands how to solve the error result in Aspen Plus.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

Based on the simulation results obtains, the supercritical process with 42:1 molar ratio and working at 350^0C and 430 bar produce 997.91kg/h of FAME. The environmental impact assessment shows the heterogeneous catalyst process show the least PEI result compare to supercritical methanol process which is indicate TRO 1552.33(with product) and TRO 1668.01(with product) respectively.

5.2 Recommendation

Process modeling and simulation using Aspen plus is significant method for the process plant design. The process should be expended and develop by using different software of plant design such as HYSYS to obtain difference value and comparative result.

Basic understanding about the thermodynamics properties of chemical reaction is critical part in process modeling plant design. More parameters should be considered in simulation process due difference chemical component give difference of thermodynamic properties that will hard to determine in the aspen plus. In addition, the by using different thermodynamic properties the will cause the result obtain is difference and affected the result of simulation.

Environment impact assessment is important for evaluation potential impact of human health and environment in order to make right decision in process design planning in early stages whether process design should be proceed or not. The assessment should be empowered by using different case study to develop good understanding and core knowledge.

Sustainability assessment covers three basic elements which is economy, environment and social. Supposedly the case study includes the economy assessment to develop valuable knowledge and experience in process design.

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